

PATENT SPECIFICATION



Application Date: Jan. 19, 1935. No. 1867/35. **452,285**

(Patent of Addition to No. 416,007: dated March 1, 1933.)

Complete Specification Left: Jan. 16, 1936.

Complete Specification Accepted: Aug. 19, 1936.

PROVISIONAL SPECIFICATION

Improvements in or relating to the Manufacture of Cyanhydrins

We, THE TRIPLEX SAFETY GLASS COMPANY LIMITED, a British Company, of 1, Albemarle Street, Piccadilly, London, W.I., and JOHN WILSON, a British Subject, of Triplex Works, Eccleshall Road, King's Norton, Birmingham, do hereby declare the nature of this invention to be as follows:—

This invention consists in improvements 10 in or relating to the manufacture of cyanhydrins of the aliphatic series.

In Specification No. 416,007 there is described the preparation of cyanhydrins of the aliphatic series, for example, acetone 15 cyanhydrin, which comprises adding to an aliphatic ketone, for example, acetone, maintained at boiling point and containing a base dissolved therein a molecular quantity of hydrocyanic acid. It has now been found that cyanhydrins of the 20 aliphatic series may also be prepared safely and efficiently by the addition to hydrocyanic acid in the liquid form, and maintained at boiling point, of a molecular 25 quantity of an aliphatic ketone, for example, acetone, the reaction being assisted by a base dissolved in the hydrocyanic acid.

Among the bases that may be employed 30 in the present process may be mentioned alcoholic caustic soda, aqueous caustic soda, gaseous ammonia, aqueous ammonia, pyridine, piperidine, one or more of the dipiperidyls, for instance the 4:4'-di-piperidyl, quinoline, primary secondary 35 or tertiary amines, potassium cyanide and sodium cyanide.

After the ketone has been added to the 40 hydrocyanic acid the mixture is maintained at boiling point for such a period as to ensure that equilibrium conditions have been attained. The time necessary to reach the equilibrium varies with the 45 nature and amount of the base used. In the case of a strong base such as caustic soda or piperidine, equilibrium is reached almost immediately. In the case of a 50 weaker base such as pyridine and using quantities such as those specified in the example which follows, it is necessary to boil for half-an-hour after the whole of the reactant has been added. In practice,

an organic base such as pyridine is preferred since with this base the tendency to side reactions is minimised. Side reactions also take place if larger quantities of weak base are used or if the boiling is continued beyond the time necessary to reach equilibrium.

The recovery of the cyanhydrin from 60 the reaction mixture may be brought about as described in Specification No. 416,007 by acidifying the mixture and distilling under reduced pressure. The acid employed for acidifying is preferably a relatively non-volatile mineral acid such as sulphuric acid and this may be added in such amount that there is present 50% more acid than is necessary to neutralise the basic compound employed in the re- 65 action.

Cyanhydrins prepared in accordance with this invention may be employed for example in the preparation of unsaturated nitriles of homologues of acrylic acid, the 75 cyanhydrin being dehydrated with a powerful dehydrating agent such as phosphorus pentoxide in the presence of a soluble base.

In the dehydrating step of the process, 80 the base and the dehydrating agent may conveniently be added to the cyanhydrin with cooling and with efficient agitation.

The conversion of the cyanhydrin to the corresponding unsaturated nitrile may be 85 carried out in accordance with the process disclosed in Specification No. 416,007.

Following is a description by way of example of one method of carrying this 90 invention into effect.

230 parts by weight of hydrocyanic acid and 20 parts by weight of pyridine (the commercially available pyridine fraction of a coal tar distillate is suitable) are placed in a large shallow vessel provided 95 with a stirrer, an efficient reflux condenser, and means, e.g. a water bath for raising the temperature and maintaining it.

The mixture of hydrocyanic acid and pyridine is raised to boiling point and 100 kept at a gentle simmer while 493 parts by weight of acetone (British Standard Specification No. 509—1933) are run in, in such a manner that the rate of boiling

is steadily maintained. After all the acetone has been added the contents are kept at boiling point for a further half-hour until equilibrium is reached.

5 The equilibrium mixture is then cooled by running cold water through the jacket. 77 parts by weight of dry pyridine are then added after which 750 parts by weight of granular phosphorus pentoxide 10 are also added while stirring and cooling. An oil bath is now substituted for the water bath and the temperature is slowly raised to about 90° C. The dehydration reaction commences, the contents begin to 15 froth and the temperature rapidly rises. During this stage a further 77 parts by weight of pyridine are added. Methacrylonitrile, acetone and hydrocyanic acid distil over. The product is fractionated 20 with approximately the following yields. 55% of the theoretical quantity of nitrile is obtained, 25% of the original acetone and hydrocyanic acid are recovered as such, and approximately 20% of the 25 original materials are lost in various side reactions including the polymerisation of hydrocyanic acid itself, acetone condensations and hydrolysis of the cyanhydrin.

Alternatively, the equilibrium mixture

after cooling by running cold water 30 through the jacket has added to it with stirring 750 parts by weight of granular phosphorus pentoxide. An oil bath is then substituted for the water bath and 77 parts by weight of dry pyridine are added. 35 The temperature rises and is assisted by heating the oil bath. When the temperature reaches approximately 90° C. the dehydration reaction commences. The subsequent steps in the process are carried 40 out as described above.

The nitrile of methacrylic acid as produced in accordance with this invention is particularly useful as a polymerisable substance for the manufacture of tough 45 transparent articles, films, filaments, adhesives, lacquers, moulding powders and thermoplastic materials.

Again, the polymerisation products may be employed in the manufacture of safety 50 glass either in the formation of the strengthening layer or as a uniting agent, cement or enamel.

Dated this 19th day of January, 1935.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Cyanhydrins

We, THE TRIPLEX SAFETY GLASS COMPANY LIMITED, a British Company, of 55 1, Albemarle Street, Piccadilly, London, W.1, and JOHN WILSON, a British Subject, of Triplex Works, Eccleshall Road, King's Norton, Birmingham, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

65 This invention consists in improvements in or relating to the manufacture of cyanhydrins of the aliphatic series.

In Specification No. 416,007 there is described the preparation of cyanhydrins 70 of the aliphatic series, for example, acetone cyanhydrin, which comprises adding to an aliphatic ketone, for example, acetone, maintained at boiling point and containing a base dissolved therein, a molecular quantity of hydrocyanic acid. It has now been found that cyanhydrins 75 of the aliphatic series may also be prepared safely and efficiently by the addition to hydrocyanic acid in the liquid form, and maintained at boiling point, of an aliphatic ketone, the reaction being assisted by a base dissolved in the hydro-

cyanic acid.

The present invention accordingly comprises a process for the manufacture of a 85 cyanhydrin of the aliphatic series which comprises adding to liquid hydrocyanic acid maintained at boiling point and containing a base dissolved therein, a molecular quantity of an aliphatic ketone. 90 Thus, in the preparation of acetone cyanhydrin there is added to hydrocyanic acid maintained at boiling point and containing a base dissolved therein, a molecular quantity of acetone. 95

Among the bases that may be employed in the present process may be mentioned caustic soda in alcoholic solution, aqueous caustic soda, gaseous ammonia, aqueous ammonia, pyridine, piperidine, one or 100 more of the dipiperidyls, for instance the 4:4'-di-piperidyl, quinoline, primary, secondary or tertiary amines, potassium cyanide and sodium cyanide.

After the ketone has been added to the 105 hydrocyanic acid the mixture is maintained at boiling point for sufficient time to ensure that equilibrium conditions have been attained. The time necessary to reach the equilibrium varies with the 110 nature and amount of the base used. In

the case of a strong base such as caustic soda or piperidine, equilibrium is reached almost immediately. In the case of a weaker base such as pyridine and using 5 quantities such as those specified in the example which follows, it is necessary to boil for half-an-hour after the whole of the reactant has been added. In practice, an organic base such as pyridine is preferred since with this base the tendency to 10 side reactions is minimised. Side reactions also take place if larger quantities of weak base are used or if the boiling is continued beyond the time necessary to 15 reach equilibrium.

The recovery of the cyanhydrin from the reaction mixture may be brought about as described in Specification No. 416,007 by acidifying the mixture and distilling 20 under reduced pressure. The acid employed for acidifying is preferably a relatively non-volatile mineral acid such as sulphuric acid and this may be added in such amount that there is present up 25 to 50% more acid than is necessary to neutralise the basic compound employed in the reaction.

Cyanhydrins prepared in accordance with this invention may be employed for 30 example in the preparation of unsaturated nitriles of homologues of acrylic acid, the cyanhydrin being dehydrated with a powerful dehydrating agent such as phosphorus pentoxide in the presence of a 35 soluble base.

In the dehydrating step of the process, the base and the dehydrating agent may conveniently be added to the cyanhydrin with cooling and with efficient agitation. 40 The conversion of the cyanhydrin to the corresponding unsaturated nitrile may be carried out in accordance with the process disclosed in Specification No. 416,007.

Following is a description by way of 45 example of one method of carrying this invention into effect.

EXAMPLE.

230 parts by weight of liquid hydrocyanic acid and 20 parts by weight of 50 pyridine (the commercially available pyridine fraction of a coal tar distillate is suitable) are placed in a large shallow vessel provided if desired with a stirrer, an efficient reflux condenser, and means, 55 e.g. a water bath for raising and maintaining the temperature.

The mixture of hydrocyanic acid and pyridine is raised to boiling point and kept at a gentle simmer while 493 parts by 60 weight of acetone (British Standard Specification No. 509—1933) are run in, in such a manner that the rate of boiling is steadily maintained. After all the acetone has been added the contents are 65 kept at boiling point for a further half-

hour until equilibrium is reached.

The pure cyanhydrin may be obtained from the equilibrium mixture after cooling by acidifying with a slight excess of sulphuric acid. The acid liquid is then 70 distilled in vacuo using the ordinary water pump. Hydrocyanic acid, water, and acetone distil over and the refractive index of the distillate rises steadily. When it reaches 1.395 the distillate is 75 almost pure cyanhydrin and is collected. The yield of material having a refractive index of 1.395 to 1.398 at 20° C. amounts to 65% of the theory.

The conversion of the acetone cyanhydrin in the equilibrium mixture to methacrylonitrile may be carried out as follows.

The equilibrium mixture is cooled by running cold water through the jacket. 77 parts by weight of dry pyridine are then added after which 750 parts by weight of granular phosphorus pentoxide are also added while stirring and cooling. An oil bath is now substituted for the water bath and the temperature is slowly raised to about 90° C. The dehydration reaction commences, the contents begin to froth and the temperature rapidly rises. During this stage a further 77 parts by 95 weight of pyridine are added. Methacrylonitrile, acetone and hydrocyanic acid distil over. The product is fractionated with approximately the following yields. 55% of the theoretical quantity of nitrile 100 is obtained, 25% of the original acetone and hydrocyanic acid are recovered as such and approximately 20% of the original materials are lost in various side reactions including the polymerisation of 105 hydrocyanic acid itself, acetone condensations and hydrolysis of the cyanhydrin.

Alternatively, the equilibrium mixture after cooling by running cold water through the jacket has added to it with 110 stirring 750 parts by weight of granular phosphorus pentoxide. An oil bath is then substituted for the water bath and 77 parts by weight of dry pyridine are added. The temperature rises and is assisted by 115 heating the oil bath. When the temperature reaches approximately 90° C. the dehydration reaction commences. The subsequent steps in the process are carried out as described above. 120

The nitrile of methacrylic acid as produced in accordance with this invention is particularly useful as a polymerisable substance for the manufacture of tough transparent articles, films, filaments, adhesives, 125 lacquers, moulding powders and thermoplastic materials.

Again, the polymerisation products may be employed in the manufacture of safety glass either in the formation of the 130

strengthening layer or as a uniting agent, cement, or enamel.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the manufacture of a cyanhydrin of the aliphatic series which comprises adding to liquid hydrocyanic acid maintained at boiling point and containing a base dissolved therein, a molecular quantity of an aliphatic ketone. 10

2. A process as claimed in Claim 1 15 wherein in the manufacture of acetone cyanhydrin the aliphatic ketone employed is acetone.

3. A process as claimed in Claim 1 or Claim 2 wherein the base comprises an 20 organic compound of the heterocyclic series.

4. A process as claimed in Claim 3 wherein the base consists of pyridine, piperidine, di-piperidyl, or quinoline. 25

5. A process as claimed in Claim 1 or Claim 2 wherein the base consists of caustic soda in alcoholic or aqueous solution or gaseous or aqueous ammonia. 30

6. A process as claimed in Claim 1 or Claim 2 wherein the base consists of potassium or sodium cyanide. 35

7. A process as claimed in any one of the preceding claims wherein after the

addition of the aliphatic ketone the mixture is maintained at boiling point for 35 such a period as to ensure that equilibrium conditions have been attained.

8. A process as claimed in any one of the preceding claims wherein the cyanhydrin is recovered from the reaction mixture by acidifying the said mixture with mineral acid, preferably a relatively non-volatile mineral acid, and distilling under reduced pressure. 40

9. A process as claimed in Claim 8 45 wherein the mineral acid employed for the recovery of the cyanhydrin consists of sulphuric acid.

10. A process as claimed in Claim 8 or Claim 9 wherein the amount of acid 50 employed is up to 50% more than is necessary to neutralise the base employed in the reaction.

11. A process for the manufacture of acetone cyanhydrin substantially as 55 described in the specific example hereinbefore set forth.

12. Cyanhydrins whenever prepared or produced by the process hereinbefore particularly described and ascertained. 60

Dated this 16th day of January, 1936.

BOULT, WADE & TENNANT.
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.